



Short communication

Silicon nitride thin film electrode for lithium-ion batteries

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HIGHLIGHTS

- Silicon nitride films formed by using pulsed laser deposition show redox reactions below 0.5 V.
- They deliver high capacities exceeding 1000 mAh g⁻¹.
- The silicon nitride films show high capacity retention in solid electrolytes.

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ABSTRACT

This paper presents electrode properties of silicon nitride (SiN_{0.92}) as a negative electrode in a lithium battery investigated in a solid electrolyte. SiN_{0.92} thin films formed by using pulsed laser deposition technique show redox reactions below 0.5 V vs. Li⁺/Li. A 200 nm thick film delivers a high capacity of 1800 mAh g⁻¹ at the first reduction process and retains 1300 mAh g⁻¹ after 100 cycles. Although increasing the film thickness to 500 nm decreases the capacity to some extent, the capacities in the 1st and 100th are 1200 and 700 mAh g⁻¹, respectively, which are quite higher than that of the current carbon negative electrode.

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1. Introduction

Recent advances in Li-ion batteries (LIB) have released various wireless devices such as cell phones, digital cameras, and laptop computers. As the amount of their information processing becomes large, the consumption of electric power remarkably increases, and thus the further increase of energy density of LIB is highly demanded. The capacity of graphite negative electrode, which is commonly used in commercially available LIBs, is approaching its theoretical limit, and further progress is expected to be brought through the usage of silicon negative electrode.

Although, Si negative electrode has been studied for many years because of its high theoretical capacity (ca. 4200 mAh g⁻¹), it has not become practicable yet. One of the large difficulties to use Si electrode in practice is its poor capacity retention, which is

attributed to the pulverization of Si negative electrode through the 300% volumetric expansion/contraction during the charge (alloying) and discharge (dealloying).

Such rapid capacity fading is a common drawback of many alloy negative electrodes. One way to overcome this difficulty is a concept so-called “alloy electrode formed in-situ from convertible oxides [1,2]”. For example, SnO is used in place of elemental Sn in the preparation of negative electrode [3]. When the electrode is charged (reduced), SnO is converted into elemental Sn with a formation of Li₂O by a so-called ‘conversion reaction’. The resultant elemental Sn is alloyed with Li in the further reduction to act as an alloy electrode, while the Li₂O buffers the volume change as a solid matrix to improve the cycling performance. This concept is indeed effective in improving the cycling performance of Si.

In the “in-situ formed alloy electrode from convertible oxide”, the conversion reaction usually takes place only once, and only the alloying and dealloying reactions proceed reversibly. On the other hand, some oxides including CoO show reversible conversion reaction [4]. Although they do not show proceeding alloying reactions, the capacities are quite high: some of them even show

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much higher capacity than conventional graphite electrodes. They are regarded as a new class of negative electrodes, called ‘conversion electrode [4–6]’. Since the in-situ formed alloy electrode deliver large capacity at the first reduction process, if the conversion process is reversible as conversion electrodes, huge capacities are anticipated.

We have synthesized a $\text{Li}_2\text{Si}_3\text{N}_3$ film by using pulsed laser deposition (PLD) method and confirmed that the conversion and alloying reactions proceed consecutively and reversibly [7]. However, the conversion reaction takes place at around 2.5 V vs. Li^+/Li , which is too noble to be used as a negative electrode reaction. This study aims at lowering the conversion reaction potential in the consecutive reactions, which may be achieved by replacing the anion from sulfide to nitride, because some transition metal nitrides show large capacities below 1 V vs. Li^+/Li [8–11].

2. Experimental

The silicon nitride formed into thin films was investigated in this study. The films were made by means of a pulsed laser deposition (PLD) system equipped with a KrF excimer laser from a sintered Si_3N_4 pellet. The laser energy was 5 mJ (0.2 J cm^{-2}) with 20 Hz repetition rate, which gives the deposition rate of 1.7 nm min^{-1} . The weight of the deposited film was monitored by using a quartz crystal microbalance (QCM, CRTM-6000, ULVAC). All films were deposited on 0.1 mm thick buffed stainless steel substrates kept at room temperature.

The charge–discharge properties of the films were investigated in two-electrode solid-state half-cells using a multi-channel potentiostat-galvanostat (PS-08, Toho-Giken). The glass ceramic solid electrolyte with the composition of $70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$ was used as the electrolyte, and Li–In alloy, which shows electrode potential of 0.62 V vs. Li^+/Li , was used as the counter electrode. The cells were cycled to charge (lithiate or reduce) and to discharge (delithiate or oxidize) the silicon nitride electrodes at constant currents. All measurements were performed under Ar atmosphere at room temperature. Note that the voltages in this paper including in the figures are expressed by adding the potential of In–Li alloy (0.62 V vs. Li^+/Li) to the cell voltages as if lithium metal were used as the counter electrode.

The surface morphologies of the films were observed by scanning electron microscopy (SEM; VE-8800, Keyence). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a scanning XPS microprobe (PHI Quantera SXM, ULVAC-PHI), which uses monochromated Al-K α radiation.

3. Results and discussion

Fig. 1(a) shows an SEM image of the 500 nm thick silicon nitride film. It is basically flat and a small number of particles are seen.

Fig. 2 shows the XPS spectra of Si 2p (a) and N 1s (b) of the silicon nitride film and the Si_3N_4 powder (Rate Metallic Co. Ltd., Japan), which are normalized for the areas of the Si 2p peaks. The peaks of Si 2p and N 1s of the silicon nitride film are located at 101.9 eV and 397.7 eV, respectively, which are close to those of the Si_3N_4 powder. There are no clear peaks corresponding to silicon or silicon oxide, which should appear at 99.5 and 103.5 eV, respectively, and thus it can be concluded that the most part of silicon atoms are nitrated and there are few Si domains in the film. The peak of the Si 2p of the silicon nitride film slightly shifts to low energy side compared to the Si_3N_4 powder, which suggests that the oxidation state of Si is lowered from +4. In fact, a large deficiency of nitrogen atoms in the film is confirmed in the XPS spectra: The film composition estimated from the peak intensities is $\text{SiN}_{0.92}$.

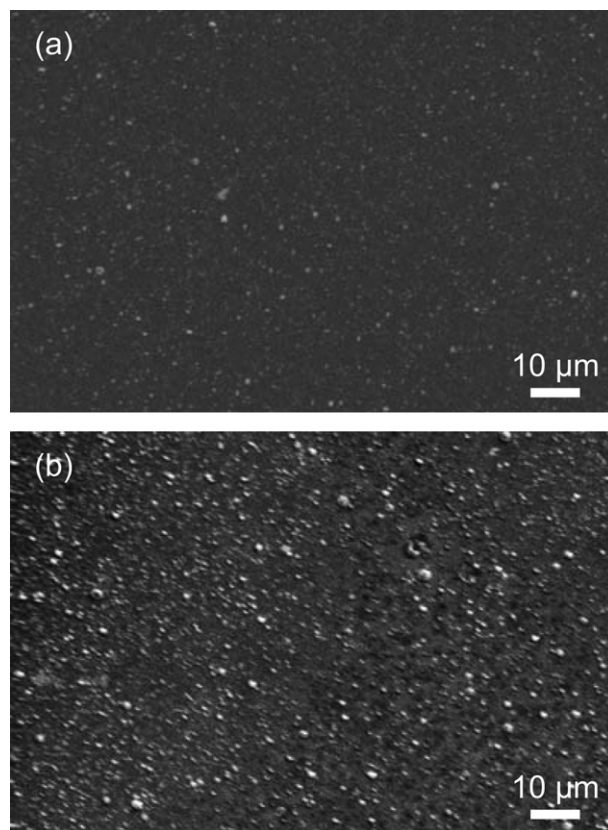
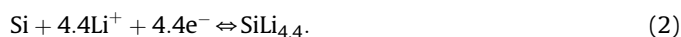
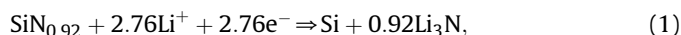


Fig. 1. SEM images for the silicon nitride films as deposited (a) and after 100 charge–discharge cycles (b).

Fig. 3 shows the charge–discharge properties of $\text{SiN}_{0.92}$ film with a thickness of about 200 nm, where the charge–discharge rates are 0.1C (charge) and 0.2C (discharge), respectively. Although Si_3N_4 has been usually regarded inactive [12,13] or very low in the activity to lithium [14], the film shows clear charge–discharge behavior. The 1st charge curve shows a potential overshoot at the initial stage of the reaction. This is characteristic of the reactions, which require nucleation of a new phase [5], including conversion reaction. After the potential overshoot, a long plateau appears at 0.1 V vs. Li^+/Li with a capacity of ca. 1800 mAh g^{-1} and an inflection point around 1000 mAh g^{-1} . The flat potential plateau in the first charge becomes slant in the following discharge, which suggests significant changes in the material during the first charge. However, the charge–discharge curves are steady in the following cycles.

The charge–discharge behavior observed here is very similar to that reported for the silicon nitride film fabricated by RF sputtering, which showed a capacity of 3000 mAh g^{-1} [15]. In the study, silicon nitrides are categorized into convertible electrode system; that is, conversion reaction from the silicon nitride to elemental silicon occurs irreversibly, followed by reversible alloying–dealloying reactions. Such reactions corresponding to the present material would be described in the following equations,



However, the coulombic efficiency in the first cycle is calculated to be about 60% on the basis of the reactions (1) and (2). On the other hand, the coulombic efficiency in the 1st cycle observed in the

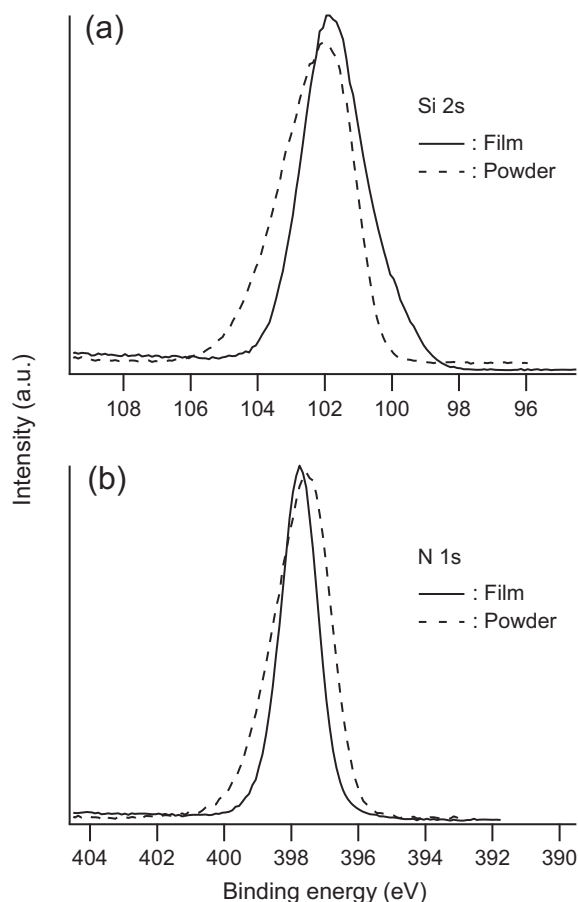


Fig. 2. XPS spectra of Si 2p (a) and N 1s (b) of the silicon nitride film and the Si_3N_4 powder. The intensities are normalized to equalize the areas of Si 2p peaks between the spectra.

present study exceeds 80%, which strongly suggests that the conversion reaction (1) is reversible and the reduction product is re-oxidized to a nitride in the first discharge process. In other words, the $\text{SiN}_{0.92}$ film has a character of conversion electrode.

If the successive reactions from (1) to (2) are reversible, the theoretical capacity is 4700 mAh g^{-1} . However, the observed capacity is only 1800 mAh g^{-1} even in the 1st charge, which is much less than the theoretical value. One of the explanations for the small

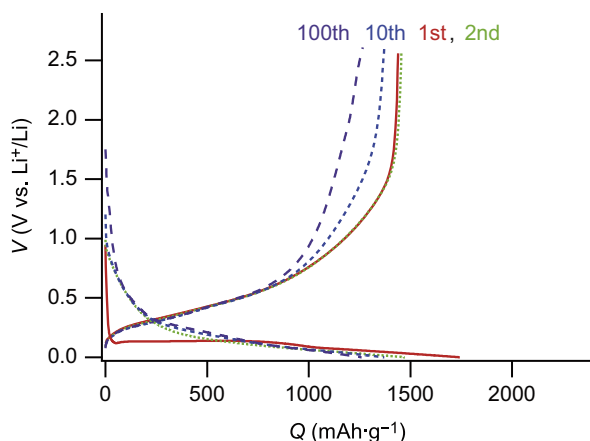


Fig. 3. Charge (0.1C)–discharge (0.2C) curves of the $\text{SiN}_{0.92}$ film. The numbers in the figure represent the cycles.

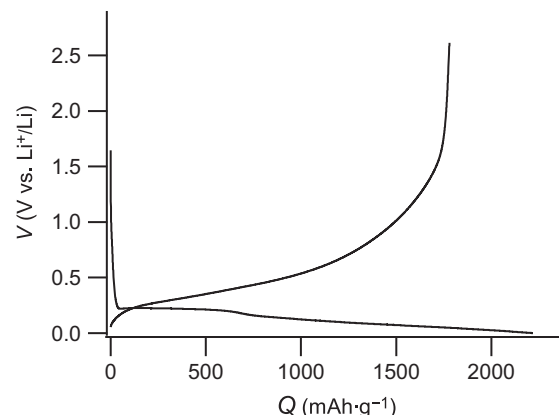


Fig. 4. Charge–discharge (0.02C) curves of the 100 nm thick $\text{SiN}_{0.92}$ film.

capacity is that only the conversion reaction (1) takes place. However, it is not reasonable, because the electrode potential reaches 10 mV vs. Li, where elemental silicon resulting from the conversion reaction should be formed into Si–Li alloys. In fact, the inflection point appearing in Fig. 3 suggests that at least two kinds of reactions proceed during the first reduction process. Another conceivable explanation is slow kinetics of the reaction; that is, low conductivity, for example, of the $\text{SiN}_{0.92}$ film results in the incomplete reaction. However, the capacity does not significantly increase, even when the thickness of the film is decreased to 100 nm and the charge–discharge rate is lowered to 0.02C, as shown in Fig. 4: the capacity delivered from the silicon nitride film is only 2200 mAh g^{-1} even under this condition, where kinetics hardly limits the capacity. These results suggest that the very small capacity is not explainable as far as reactions (1) and (2) hold.

Silicon nitride will be reduced to elemental Si in the conversion reaction, and then alloying reaction will proceed undoubtedly. On the other hand, the byproduct in the conversion reaction may not be Li_3N . In fact, change in the Gibbs free energy (ΔG) in the conversion reaction from Si_3N_4 to Si with the formation of Li_3N as the byproduct calculated from the thermodynamic data of the materials is 130 kJ mol^{-1} ; the positive value indicates that the conversion reaction does not occur spontaneously.

Because small formation energy of Li_3N results in the positive ΔG , it is more plausible to consider that more stable compounds are formed instead. One of the conceivable compounds is a lithium silicon nitride, in which strong covalent bonds between Si and N

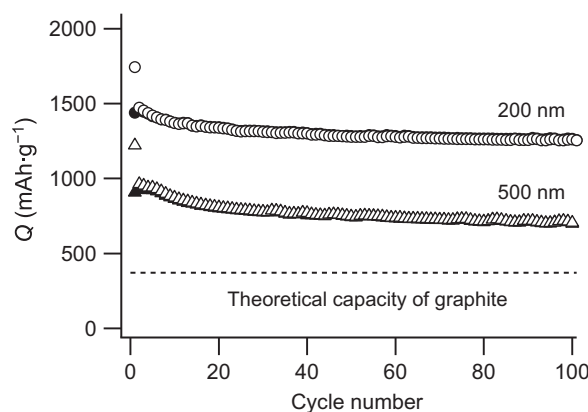
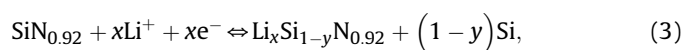


Fig. 5. Cyclability of the $\text{SiN}_{0.92}$ films and the Si films for 200 nm and 500 nm thick films. Open and closed symbols indicate the capacities in the charge and discharge, respectively.

will raise the formation energy and make the ΔG negative. That is, the electrode reaction can be expressed in the following equations:



There have been reported several phases in Li–Si–N ternary system [16]. When the ternary compound is assumed to be Li_2SiN_2 , i.e. $x = 0.92$ and $y = 0.54$ are assumed in the Equation (3), the reactions (3) and (4) give a theoretical capacity of 2160 mAh g^{-1} . This value agrees with the capacity observed in Fig. 4 (2200 mAh g^{-1}), i.e. for the thinnest film at the lowest rate in this study, where the kinetics hardly governs the observed capacity. Other Li–Si–N compounds may not be appropriate, because their theoretical capacities are much different (e.g., 1350 mAh g^{-1} for LiSi_2N_3 and 3000 mAh g^{-1} for Li_5SiN_3).

Although the specific capacity of Si_3N_4 is lower than the capacity that can be expected from the 4 and 4.4-electron reactions for Si in the conversion and alloying processes, respectively, the capacity is still much higher than that can be achieved in carbonaceous materials. In addition, cycling performance of Si_3N_4 is fairly good. Fig. 5 shows the cycling properties of the 200 nm and 500 nm thick $\text{SiN}_{0.92}$ films. Both films show good cyclability, and the capacities are almost constant over the 100 cycles. The 200 nm thick $\text{SiN}_{0.92}$ film gives a charge capacity as high as 1800 mAh g^{-1} at the first charge and retains 1300 mAh g^{-1} after the 100 cycles. When the film thickness is 500 nm, the initial charge capacity is as low as 1200 mAh g^{-1} ; nevertheless it retains 700 mAh g^{-1} after 100 cycles.

The high capacity retention can be indeed attributed to the solid matrix effect, which is often observed in in-situ formed alloy systems. Fig. 1(b) shows an SEM image of the 500 nm thick $\text{SiN}_{0.92}$ film after 100 cycles. Although many cracks usually appear in pure Si films after the charge–discharge reactions [17,18], few cracks are seen in the $\text{SiN}_{0.92}$ film besides particles and lumps on the surface, which are the residuals of solid electrolyte. It indicates that the tension through the volumetric change during charge/discharge is mediated in the $\text{SiN}_{0.92}$ film to bring about the good cyclability. Moreover, the silicon nitride films are cycled in solid-state cells, which also contribute to the high capacity retention, because side reactions are effectively suppressed in solid electrolytes.

4. Conclusion

The silicon nitride ($\text{SiN}_{0.92}$) films investigated in this study deliver high capacities at less noble potential below 0.5 V vs. Li^+/Li and show small capacity fading upon the cycling. These properties demonstrate that lithium nitrides are promising candidates for high capacity negative electrodes in lithium batteries.

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